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A KOMUNIKAČNÍCH TECHNOLOGIÍ

DEPARTMENT OF FOREIGN LANGUAGES
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TECHNOLOGIES FOR PORTABLE STORAGE OF ELECTRICAL ENERGY
TECHNOLOGIE PRO MOBILNÍ USKLADNĚNÍ ELEKTRICKÉ ENERGIE

BACHELOR'S THESIS
BAKALÁŘSKÁ PRÁCE

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Bakalářská práce

bakalářský studijní obor **Angličtina v elektrotechnice a informatice**
Ústav jazyků

Student: Radim Helma ***ID:*** 177768
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NÁZEV TÉMATU:

Technologie pro mobilní uskladnění elektrické energie

POKYNY PRO VYPRACOVÁNÍ:

V současné době je třeba řešit problematiku uskladnění elektrické energie v nejrůznějších mobilních zařízeních, od mobilních telefonů přes ruční nářadí po elektromobily.
Vypracujte rešerši na téma systémů pro ukládání elektrické energie v mobilních zařízeních. Zaměřte se zejména na elektrochemické systémy (baterie, akumulátory, palivové články). Stručně shrňte historii, zaměřte se na současný stav a rozveďte technologie s výhledem do budoucna a možné směry dalšího vývoje. Věnujte se i problematice elektromobilů a elektromobility obecně, shrňte historii, problémy, současnost a perspektivy.

DOPORUČENÁ LITERATURA:

LINDEN, D., REDDY, T.B. Handbook of batteries - third edition. McGraw-Hill Handbooks, 2001. 1454 p. ISBN 0-07-135978-8

Fuel Cell Handbook (Seventh Edition), EG&G Technical Services, Inc., U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory

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doc. PhDr. Milena Krhutová, Ph.D.
předseda oborové rady

ABSTRACT

The aim of this thesis is to list and compare different methods of storing electrical energy. I have combined many data sources in order to produce a brief summary of history, current problems and future possibilities for each. technology. My thesis provides the reader with a summary of factographic information on the subject of rechargeable batteries, fuel cells, supercapacitors and flow batteries.

KEYWORDS

Rechargeable battery, lithium battery, nickel–metal hydride battery, lead–acid, lithium–sulfur battery, fuel cell, flow battery, supercapacitor

ABSTRAKT

Cílem této semestrální práce je vypracovat rešerši na téma různých metod uskladnění elektrické energie. V práci jsem zkombinoval mnoho datových zdrojů a pro každou technologii jsem vytvořil stručný popis historie, současných problémů a možností do budoucna. Má práce čtenáři poskytne přehled faktografických informací na téma akumulátorů, palivových článků, superkondenzátorů a průtokových baterií. Příslušné technologie jsou uspořádány jako strukturovaný, kategorizovaný seznam.

KLÍČOVÁ SLOVA

Akumulátor, lithiový akumulátor, olověný akumulátor, lithium-sírový akumulátor, Nikl-metal hydridový akumulátor, palivový článek, prútoková baterie, superkondenzátor

PROHLÁŠENÍ AUTORA

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V Brně dne ....

(podpis autora)

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Introduction

The increasing effort of governments and the public to slow down global warming and to reduce greenhouse emissions are pressing scientists to develop better ways to store electrical energy. Debates about the limited fossil fuel reserves and their eventual depletion are currently a heated topic, but no matter what their outcome will be, people are starting to realize that the reserves are not infinite. The public is starting to push towards a shift from internal combustion engines to the more efficient and environmentally friendly electric engines. The rapid expansion of portable electronics and electric cars in recent years highlights the problems with our limited capabilities to effectively store large amounts of electrical energy.

While the newer generations of li-ion batteries might be suitable for long distance driving, car models from just two years ago do not have high enough energy density to endure such travel, especially in bigger states or cross country trips. The average lower-end electric cars have their effective range as low as 150-200 kilometers on a fully charged battery, while the higher end Tesla models manage up to 400 kilometers on a fully charged battery.

Another problem lies within infrastructure. The amount of charging stations is not that high and most of them only provide 7kW chargers, with which recharging might take upwards of a few hours to fully charge up your car’s battery. Unless you drive a high-end Tesla and happen upon a few 22kW charger stations on the way, longer trips are out of the question.

Renewable energy suffers because of insufficient energy storage as well. Due to the inconsistencies in weather, large scale wind and solar farms will require equally massive energy storage.

Energy density is one of the most important characteristics of batteries as it describes the ratio of energy to mass. In the following figure, I have merged data from different sources cited in bibliography to depict the theoretical and currently achieved energy density of materials used for energy storage. If not stated otherwise, gravimetric energy density with units of Wh/kg is used.

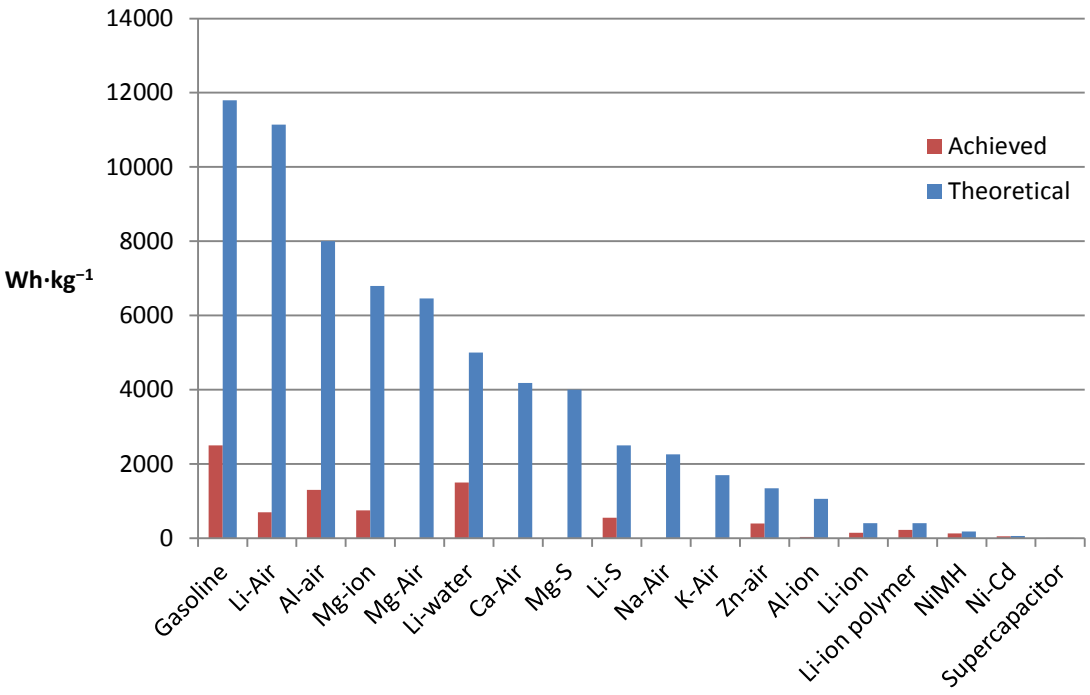

Fig. 1 – Energy density comparison (note that some of these are primary cells) [5] [11][12]

As we can clearly see, there is plenty of research to be done and experiments to be run in order to achieve the maximum potential of each technology. In my thesis, I will briefly outline the history of electrochemical systems as well as the contemporary technologies, describe their strengths and weaknesses and the possibilities of future development.

In English language, the word “battery” is used for both disposable and rechargeable batteries. To avoid confusion, batteries are divided into so called primary and secondary batteries respectively. [1]

Although this thesis primarily deals with different secondary cells, I have dedicated several chapters to more unconventional means of energy storage, such as supercapacitors, flow batteries and fuel cells.

There have been major breakthroughs in lithium–sulfur and lithium-ion polymer batteries in recent years. These new technologies are well on their way to replace the slowly aging Li-ion batteries. The current goal of many scientists working in this field is to achieve energy density comparable to that of gasoline. Although a noble effort, none of the accumulators listed in fig. 1 are even close to achieving that.

Lithium-seawater might look like they are the most efficient technology at the moment but their severe downside of being a primary cell and having to be submerged into sea water makes this battery unusable for everyday use. Because this thesis deals with secondary cells only, li-water battery will not be covered any further.

Rechargeable batteries have come a long way since their initial invention by Gaston Planté in 1859. Early batteries were simple, inefficient and bulky contraptions that have been pushed to their absolute limits through the years of innovations.

A lot of attention is being paid to the development of flow batteries. Although the technology is not by any means new, some major breakthroughs have been made in the field of aqueous redox batteries, these are covered in chapter 5.3.

Among the new technologies, there are supercapacitors using carbon based cathodes and lithium anodes, among other combinations. Supercapacitors on their own will most likely never replace electrochemical accumulators, they might however be used in conjunction with regular secondary cells, to increase their efficiency and cycle life. Fuel cells have been included in this thesis as well, although they do not fit under the category of secondary cells, they are a too important of a technology not to be included as a separate chapter,

1. Principle of energy storage

Battery is a device that converts chemical energy stored in the material into electrical energy and thus a source of electrical energy which provides a circuit with a potential difference. In a battery, electrons are transferred through a connected circuit from anode to cathode during discharge and from cathode to anode while charging. The electroneutrality is achieved by ions transferring through the electrolyte from one electrode to the other. [2]

The way the battery can store this energy is called the oxidation and reduction reaction. In very basic terms, oxidation means the loss of electrons and reduction means the gain of electrons. The theoretical chemical reaction is as follows. [3]

$$\text{oxidant} + \text{n}\,e^- \rightarrow \text{Reductant}$$

$$\text{Reductant} \rightarrow \text{oxidant} + \text{n}\,e^-$$

Since the two reactions are so closely connected, we call the whole process the redox reaction. The oxidizing and reducing elements are picked based on their electron surplus or electron deficit. Arguably the best reducing element is lithium. It is highly reactive and has relatively high surplus of electrons while providing the largest energy density per weight. In primary batteries, lithium is used as an anode. Such batteries are called lithium-metal batteries and are disposable. In li-ion batteries, however, we use graphite as an anode with either cobalt or manganese based cathode. [4]

In order to avoid redundancy, only the discharging reaction will be written in the following chapters. To produce a charging reaction, we only need to reverse the charging one, since the reactions in secondary cells must be by definition reversible.

The following figure (Fig. 2) shows an illustration of a lithium-ion battery (with graphite as an anode and Lithium cobalt oxide as a cathode) undergoing the reduction oxidation reaction.

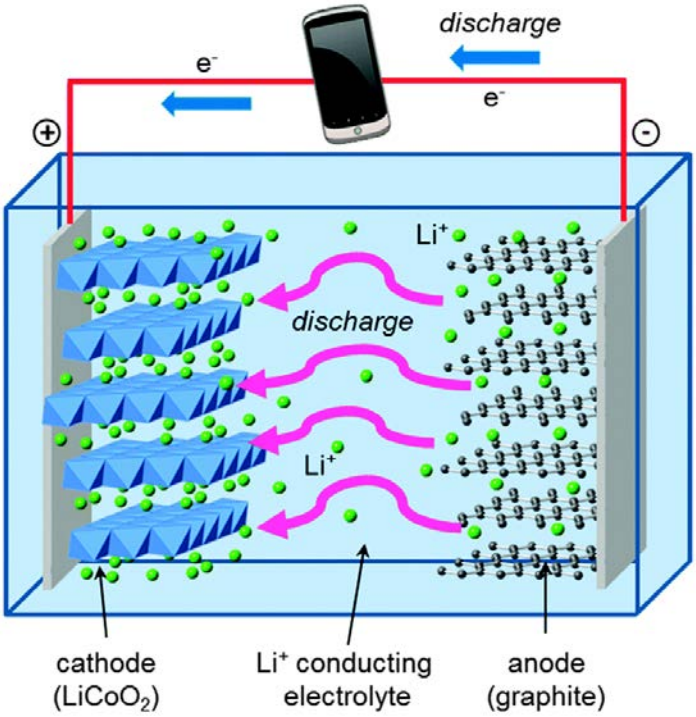

Fig. 2 - LiCoO2 Redox discharging [5]

During charging, a voltage applied across the electrodes forces lithium ions to be extracted from the LiCoO2 crystal. These ions diffuse through the electrolyte, and are intercalated between the graphite sheets in the anode material. During discharge, Li ions return to the cathode via the electronically insulating electrolyte, with electrons passing around the external circuit providing useful power for the device. More about this type of battery is found in chapter 2.1. [5]

Basic principles of batteries have been devised hundreds of years ago and have not changed much since. The only components changing are the materials used for cathode, anode, electrolyte and the redox reaction used in order to store energy. The following chapters will address the material combinations of some more common batteries, as well as some newly discovered technologies that are on the rise.

1.1 Accumulator terminology

This chapter contains a list of basic terms with their definitions and explanations. These terms are needed to fully understand the contents of the following chapters.

Energy density: as already stated in the introduction, energy density describes the energy stored in a given system per unit volume(volumetric) or mass(gravimetric). Gravimetric energy density is used in the following chapters without exception.

Nominal voltage: A system is assigned a nominal voltage so that it can be conveniently designated to its voltage class. E.g. A cell with the nominal voltage of 2V might in reality have voltage of 1.8-2.2V. Nominal voltage is not measured, it is only used for description.

Cutoff voltage: A voltage at which a cell is considered to be fully discharged. Any further discharge will have a negative impact on cell's cycle life and capacity. Outside specific research conditions, some form of protection against discharge further than cutoff voltage is implemented to stop cells from getting damaged.

Potential: Real value of potential difference that is measured between cell's terminals. This value usually varies with different levels of charge. E.g. A cell charged up to 100% will output 2.0V but at 50%, the output might be 1.9V

Nernst equation: $E = E^0 + \frac{0.05916}{z} log_{10} \frac{a_{Ox}}{a_{Red}}$ where $\mathrm{E} = \text{cell potential}; \mathrm{E}^0 = \text{standard cell potential}; \frac{\mathrm{a_{Ox}}}{\mathrm{a_{Red}}} = \text{reacion quotient}$; z= number of moles of electrons transferred in the half-reaction or overall reaction. It us used to derive the reduction potential of a cell at a standard temperature(25 °C). Although the equation is not used in this thesis directly, nearly all works cited contain some form of this calculation.

Efficiency(coulombic efficiency): Expressed as a ratio between input energy and output energy. Generally given in percents. These inefficiencies occur when elements in a cell undergo an unwanted reaction or when in a fuel cell electrons pass through a membrane without doing work.

Self-discharge rate: A value that is closely associated with coulombic efficiency. It . Self-discharge rate varies in order of magnitude based on the technology used. Some lithium based batteries have a self-discharge rate of 10% per month, supercapacitors on the other hand fully discharge in a matter of minutes.

Cycle life: Expresses the number of full charge/discharge cycles that have to occur in order for the cell to reach 80%(unless stated otherwise) of the initial capacity. Some values in the following chapters have cycle life marked with "MAX", this means that little to no loss of capacity happens further beyond this point. Loss of capacity is not linear and the rate of loss decreases with time. For some systems, cycle life is also dependent on operating temperature.

2. Lithium accumulators

The most amount of research, currently, is dedicated to the study of lithium accumulators and their properties. Researchers are trying to find new material combinations and manufacturing techniques in order to develop new batteries with the best performance.

Lithium based accumulators are a great choice for applications requiring low weight and a high variety of shapes due to their excellent power-to-weight ratio and modularity.

The low atomic weight of lithium enables batteries using this technology to be used in such situations where weight matters, such as portable electronics, electric mobility equipment, tools and electric vehicles. The recharge time of 2-4 hours, constant voltage output of 3-4 volts and variable self-discharge rate of 1-10% per month depends heavily on the metal oxide used.

Lithium based batteries have many indisputable advantages. They are very flexible as far as the materials used for the electrodes are concerned. This makes them very customizable for specific situations, hence the reason why lithium based batteries are used in such a broad spectrum of applications.

Among the disadvantages are the manufacturing costs and their limited life span no matter if they are being used or not, losing around 30 percent of maximum capacity after 1000 cycles. Their high temperature sensitivity negatively affects the life span as well, making the degradation process even faster. [6]

There had also been quite a big uproar about lithium based accumulators not being safe and sometimes exploding without warning. While certain unfortunate mobile manufacturer admitted that some of their phone batteries might exhibit such behavior, its sole reason is manufacturing defect. Simply said, the advantages overshadow the disadvantages so much so that lithium batteries are the best performing accumulators currently available on the market for the use with portable electronics as well as electric vehicles.

Battery type	Theoretical energy density	Achieved energy density	Potential	Charge time	Cyles	Self discharge
	Wh/Kg	Wh/Kg	Volts		80%	%/month
Li-S	2500	550	2.1			
Li-ion	406	145	3.5-4	2-4 h	1-8,000	10%
Li-ion polymer	406	225	3.7-4.2	2-4 h	300-500	5-10%

Tab. 2.0.1 – Properties of lithium accumulators [2][5][6]

2.1 Lithium cobalt oxide

The most widespread battery combination of materials in lithium batteries and one of the two basic types is the lithium cobalt oxide battery. It combines lithium cobalt oxide, or $LiCoO_2$ as the positive electrode and graphite as a negative electrode. This combination offers large energy density while remaining compact and lightweight at a cost of safety risks.

When the outer casing gets damaged and the battery short circuits, the heated up lithium layer gets exposed to oxygen and reacts violently. Another safety concern is the relatively low thermal stability. At the temperature of only 120 °C, an uncontrollable thermal runaway might occur. To prevent this problem, the circuit in most lithium cobalt oxide batteries shuts down when the temperatures hit 90 °C as well as when a short circuit occurs.

Even with these safety precautions, manufacturing errors still happen which makes this battery inherently unsafe for applications where reliability is a high priority, such as medical sector and the military. [7]

Reaction on cathode:

$$\mathbf{LiCoO_2 - Li^+ - e^- \leftrightarrow Li_{0.5}CoO_2} \quad (2.1.1)$$

Reaction on anode:

$$\mathbf{6C + Li^+ + e^- \leftrightarrow LiC_6} \quad (2.1.2)$$

Overall:

$$\mathbf{C + LiCoO_2 \leftrightarrow LiC_6 + Li_{0.5}CoO_2} \quad (2.1.3)$$

The use of lithium cobalt oxide provides exceptional electrical performance while being rather easy to produce and the use of graphite carbon offers much higher specific energy and improved cycle life over its predecessors which were using coke. All this combined makes li-cobalt battery [1]

A good amount of research also went into the development of a doped cobalt electrode with different compounds in the effort to design a battery with better properties than when using cobalt oxide in its pure form. These mixtures often use one of the following elements: nickel, aluminium, boron and magnesium. The effects this doping has are highly dependent on the amount of cobalt replaced with the other metal. C. Julien describes the effect of doping with aluminium as such:

"Replacing a small amount of Co with Al exhibits higher voltage than the $LiCoO_2$ electrode and slightly decreases the cell capacity. At the cut-off voltage of 4.4 V, the charge gravimetric capacity of the $Li//\ LiCo_{0.95}Al_{0.05}O_2$ cell is ca. 150 mA h/g, which is a value similar to that delivered by LiCoO2 cathode." [8]

Julien later describes that the effect is substantially more noticeable when using the cobalt-aluminium ratio of more than 9:1(subscripts in the quote show the percentage of material used). In the paper he determines that for the optimal gravimetric capacity and life cycle the ratio is precisely 5:1 as the battery using such ratio managed to outperform every other sample used in the study.

2.2 Lithium Manganese Oxide

In 1996, researchers discovered a new type of cathode material for lithium-ion batteries, manganese oxide. The use of manganese oxide based cathode provides several benefits over their cobalt counterparts. Their thermal stability is excellent, they are much safer, allow for faster charging and discharging with currents of up to 30A. Their nominal voltage stays comparable with that of cobalt but they unfortunately suffer from low energy density which is approximately 50% as well as limited life span depending on their usage.

Lithium manganese oxide battery exists in two main variations: cylindrical $\mathbf{LiMn_2O_4}$ and layered $\mathbf{Li_2MnO_3}$. Although the battery can be used in the "pouch" version, same as $\mathbf{LiCoO_2}$, the vast majority of recent studies focus on the spinel version. [14]

Overall cell reaction:

$$\mathbf{Li_xMn_2O_4 + Li_yC_6 \leftrightarrow Li_{x+\delta}Mn_2O_4 + Li_{Y-\delta}C_6} \quad (2.2.1)$$

Lithium manganese oxide and cobalt oxide can be combined together in order to create $\mathbf{LiNiMnCoO_2}$(NMC). This blend of different cathode materials allows for the resulting cell to have a capacity of up to 80% of cobalt oxide while retaining the benefits of manganese oxide. The trade-off of this improved capacity is shorter life span.

2.3 Lithium-sulphur

In lithium-sulphur batteries, lithium is used to form the anode and sulphur rods coated with carbon are used as a cathode of most batteries of this type. Creating a sulfur based cathode in a lithium battery is arguably one of the best materials to use. Low costs and plenty of sulfur on earth make this line of research very attractive. Unfortunately, there are many problems associated with this technology. The following quote taken directly from the journal Materials Today describes some of the problems (p. 259).

"S based cathodes suffer from low potential vs. Li/Li^+, low electrical conductivity, dissolution of intermediate reaction products (polysulfides) in electrolyte, and (in the case of pure S) very low vaporization temperature, which induces S loss while drying the electrodes under vacuum. Sulfur also suffers from ~80% volume change, which may destroy the electrical contact in standard carbon composite electrodes."

Authors later state that in order to counteract the effects of dissolution and expansion, the S electrode is locked into a hollow structure made out of polyvidone(PVP), carbon or other materials. [9]

Reduction of polysulfides:

$$\boldsymbol{S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3} \quad (2.3.1)$$

Diffusion:

$$\boldsymbol{Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8} \quad (2.3.2)$$

The Li-S battery is still in its experimental stages as researchers are trying to eliminate the electrode degradation issues. Lithium-sulphur batteries promise up to five times better performance than the currently used lithium cobalt oxide batteries, once these problems are resolved.

3. Other accumulators

This chapter includes all major accumulators that use some kind redox reaction, with the exception of li-ion batteries from previous chapters.

Battery type	Theoretical energy density	Achieved energy density	Potential	Charge time	Cyles	Self discharge
	Wh/Kg	Wh/Kg	Volts		80%	%/month
Mg-ion	6800	750	0.8-2.38		>2,000	
Zn-air	1350	400	1.5-1.65		10,000	
Al-ion	1060	40	2.6	1 min	6,500 +	
NiMH	180	135	1.25	2-4 h	300-500	30%
Alkaline rechargeable	125	80	1.4-1.5	2-3 h	50	0.30%
Ni-Cd	60	50	1.25	1 h	1,500	20%
Pb acid	33	42	2	8-16 h	200-300	5%

Tab. 3.0.1 - Properties of electrochemical accumulators [3][4][10][12]

3.1 Lead–acid

Lead-acid battery is by far the oldest battery on the list. It was discovered more than 150 years ago and it is still is one of the most widespread actively used battery types. However, it has been severely modified and improved since its initial inception. The performance of this specific type of battery is rather poor when compared with other, more modern types, but they are prized for their low manufacturing cost, stable performance with temperature change and the ability to provide large bursts of current in a short period of time. For these reasons, lead-acid batteries are widely used in the automotive industry as so called SLI(starting, lighting, ignition) batteries. [1]

The structure consists of a hard container, usually made from plastic with up to six voltaic cells connected in a series. Each cell produces 2 volts and comprises finely divided lead($\mathbf{Pb_{(s)}}$) in a frame made out of porous plate of metallic lead as the anode and a lead frame covered with lead dioxide($\mathbf{PbO_{2(s)}}$) serving as the cathode. Sulfuric acid($\mathbf{H_2SO_4}$) is used as an electrolyte.

According to ausetute.com.au, the discharging redox reaction of the voltaic cell goes as follows: [10]

$$\mathbf{Pb_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO_4{}^{2-}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O} \quad (3.1.1)$$

As the lead-acid cell discharges: $\mathbf{2PbSO_4}$ precipitates out and deposits on both the anode and the cathode. $\mathbf{H^+}$ from the electrolyte $\mathbf{H_2SO_{4(aq)}}$ is being used to produce water at the cathode. Concentration of $\mathbf{H^+}$ will be decreased over time (concentration of $\mathbf{H_2SO_{4(aq)}}$ decreases). pH of the electrolyte $\mathbf{H_2SO_{4(aq)}}$ will increase.

When recharging, the $\mathbf{2PbSO_{4(s)}}$ on each electrode is removed. Concentration of $\mathbf{H^+}$ increases. pH of the electrolyte $\mathbf{H_2SO_{4(aq)}}$ decreases. [10]

The recharging process is as follows:

$$\mathbf{2PbSO_{4(s)} + 2H_2O_l \rightarrow Pb_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO_4{}^{2-}_{(aq)}} \quad (3.1.2)$$

3.2 Nickel–cadmium

The NiCd battery is a direct predecessor of the newer nickel-metal hydride battery. Having been invented more than a hundred years ago, nickel-cadmium batteries have gone through a lot of changes during their lifetime. Although this technology was mostly overlooked at the time of its discovery, it started to be widely used when the fully sealed version was developed. The battery consisted of nickel hydroxide (NiOOH) as the positive electrode and metallic cadmium (Cd) as negative electrode. The electrolyte also went through some advances until manufacturers settled on a solution of potassium hydroxide (KOH). [1]

During the discharge reaction, cadmium metal oxidizes to cadmium hydroxide and releases two electrons:

$$\mathbf{Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e} \quad (3.2.1)$$

Simultaneously, the nickel oxide gets reduced to nickel hydroxide and accepts an electron:

$$\mathbf{NiOOH + H_2O + e \rightarrow OH^- + Ni(OH)_2} \quad (3.2.2)$$

The overall reaction can be written as following:

$$\mathbf{Cd + 2NiOOH + 2H_2O \rightarrow Cd(OH)_2 + 2}\boldsymbol{Ni(OH)_2} \quad (3.2.3)$$

With a nominal voltage of 1.2V produced by each cell and due to the lack of suitable alternatives, they were largely popular to use in a wide variety of applications from household electronics to cameras and even as an emergency power supply. They were rapidly replaced by nickel–metal batteries when said batteries became more affordable and easier to produce.

3.3 Nickel–metal hydride

Nickel-metal hydride is a successor to the Nickel–cadmium battery. The main difference between the two is the use of a much safer hydrogen-absorbing alloy inside of the NiMH batteries instead of cadmium. These batteries have undergone much development over the years and are now used for a wide range of products from electronics to electric vehicles.

The use of metal hydride had more than doubled the energy density on the negative metal hydride electrode, effectively halving its volume when compared to cadmium. This means increased volume for the positive nickel electrode and therefore increased

overall capacity and cycle life. Potassium hydroxide is used as an electrolyte due to its high ionic conductivity and low manufacturing costs.

Nickel oxyhydroxide is the active metal in a charged state. The negative active material, in the charged state, is hydrogen in the form of a metal hydride. The reaction is completely reversible as the hydrogen gets absorbed by the metal alloy during charging and dispersed during discharge. The chemical reactions on each electrode go as follows: [1]

During discharge, the nickel onyhydroxide is reduced to nickel hydroxide

$$\mathbf{NiOOH + H_2O + e \rightarrow Ni(OH)_2 + OH^-} \qquad \mathbf{E = 0.52V} \tag{3.3.1}$$

Simultaneously, the metal hydride MH is oxidized into the metal alloy M

$$\mathbf{MH - OH^- \rightarrow M + H_2O + e} \qquad \mathbf{E = 0.83V} \tag{3.3.2}$$

The overall discharge reaction

$$\mathbf{MH + NiOOH \rightarrow M - Ni(OH)_2} \qquad \mathbf{E = 1.35V} \tag{3.3.3}$$

The recharging process is identical but with reversed reactions.

4. Alternative energy storage

This chapter contains energy storage technologies that did not fit any of the previous chapters. These include: Fuel cells, supercapacitors and flow batteries.

4.1 Fuel cell

Fuel cell is a type of galvanic cell that continuously creates electrical energy by oxidizing fuel and releasing the stored chemical energy in that fuel. In its fundamental components, it is very similar to a conventional redox flow battery. The difference is in the fact that a fuel cell requires a constant intake of fuel and oxidant from outside sources in order to keep providing energy. The fuel cell itself does not technically store energy, the energy is stored in the fuel.

In contrast with redox batteries, the anode material of a fuel cell is usually either gas or liquid. The anode materials include: hydrogen, methanol and natural gas. The following example depicts a solid oxide fuel cell with oxygen from air serving as oxidant and hydrogen as fuel.

Both electrodes contain catalysts that induce the oxidation reaction of the fuel. The products of this reaction are negatively charged oxygen ions and electrons. At the same time, the hydrogen ions are pulled through the electrolyte and the electrons flow through an external circuit generating somewhere from 0.71 to 1.23 V depending on conditions and type of fuel and oxidant used. In this case, the byproduct of these reactions is water and heat. [1] The whole process can be seen in fig. 3.

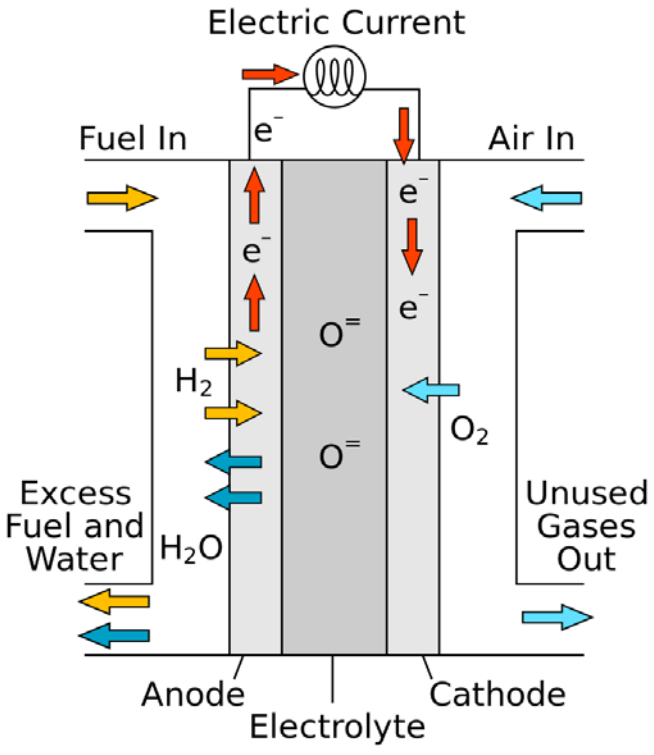

Fig. 3 - Fuel cell scheme [13]

Anode reaction:

$$\mathbf{2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-} \quad (4.1.1)$$

Cathode reaction:

$$\mathbf{O_2 + 4e^- \rightarrow 2O^{2-}} \quad (4.1.2)$$

Overall reaction:

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O} \quad (4.1.3)$$

Fuel cells are distinguished by the electrolyte they use. Here are some of the electrolytes used: Aqueous alkaline solution, polymer membrane, humic acid, ceramic(used in example and fig.3), salt water and many others.

Efficiency varies across different types of fuel cells, but the average is 40-60%. Theoretical efficiency may go up to 85% if there is such a setup that recycles unused fuel and also takes advantage of the heat generated by the reactions. [13]

4.2 Supercapacitor

Supercapacitor is a blend between conventional capacitors and batteries. It is an energy storage system designed to allow for high capacitance and to store and provide energy at high rates, when compared to regular batteries. Capacitance is directly proportional to the surface area of electrodes. Because of this surface area requirement, a material such as activated carbon is used due to its porous structure. Recent developments in more effective manufacturing of carbon nanomaterials made creation of better performing supercapacitors possible. Carbon nanotubes are an excellent choice because of their exceptional mechanical and electrical properties, namely their high surface area and good conductivity. [18]

A supercapacitor can store the charge in two ways: electrostatically and electrochemically.

An **electrostatic** supercapacitor stores charge using the reversible absorption of ions from the electrolyte onto an active material with a high accessible specific surface area(typically carbon based).

An **electrochemical** supercapacitor is more akin to a battery than a capacitor. It uses a fast faradaic reduction oxidation reaction to store charge. The device consists of two porous plates kept apart by a layer of electrolyte with a ion permeable membrane in the middle. Electrochemical supercapacitors are generally the most used type.

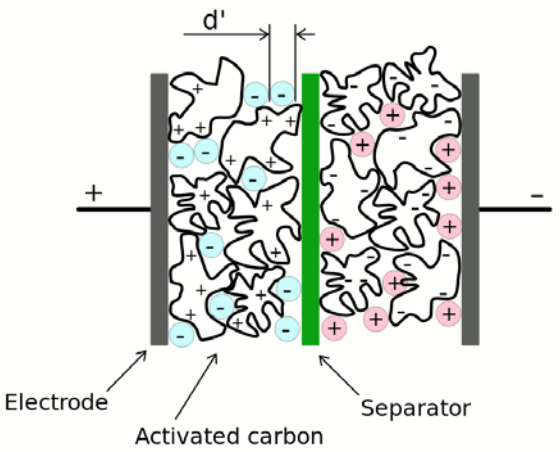

Fig. 5 - Structure of an electrochemical double layer supercapacitor [18]

In a paper from 2009, Chinese researchers used a gas-solid reduction process to produce a new 2D graphene material out of which electrodes were created. This new method of carbon nanotube electrode preparation allowed for a specific capacitance of 205F/g at 1V and energy density of 28.5 Wh/kg at the cost of a shorter cycle life. [17]

A **hybrid** supercapacitor combines the two previous types into one. It is constructed with one electrode being predominantly electrostatic and the other electrochemical. A lot of attention was focused on this type of supercapacitor because of energy density limitations of both electrochemical and electrostatic systems. An example that had undergone a lot of testing and innovation in recent years is the lithium-ion capacitor. [19]

4.2.1 Lithium-ion capacitor(Li-HEC)

As a way of improving energy density of supercapacitors without negatively impacting cycle life, a strategy involving the combination of a supercapacitor electrode with li-ion battery electrode. This combination resulted in a mixed device that exhibits the advantages of both li-ion batteries and supercapacitors. All the while retaining high power density(unlike EDLCs) as well as moderate energy density.

Using $Li_4Ti_5O_{12}$ as Li-insertion type anode and high surface area porous carbon (HSPC) as cathode, researchers in 2014 were able to create Li-HEC with a maximum energy density of ~55 Wh/kg all the while preserving a very high columbic efficiency of over 95% at high current rates and stabilized capacity after 2000 cycles ar around 87% of the original value. [20]

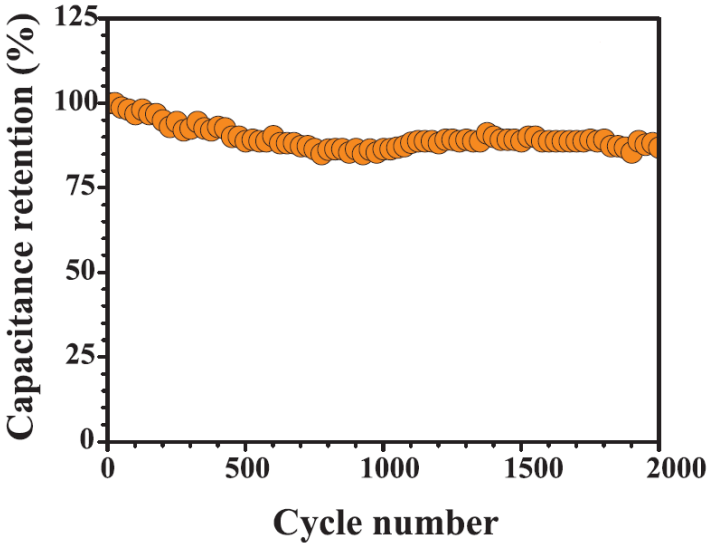

Fig. 6 - Cycle life of formentioned supercapacitor [20]

The chief problem with supercapacitors and the reason why they are not more widely employed is their low energy density and low operational voltage and high cost. Recent research and development in this field seems to have solved many at least the first two of these issues using both carbon nanostructure and activate charcoal approach.

4.3 Flow battery

A flow battery is an electrochemical system in which energy is stored in tanks of liquid that are separated by a permeable membrane which allows for ionic exchange to take place. The working principle and liquid solutions differ based on what properties are desirable. The three leading technologies in this line of research are zinc-bromine, vanadium-redox and regenesys systems. [15]

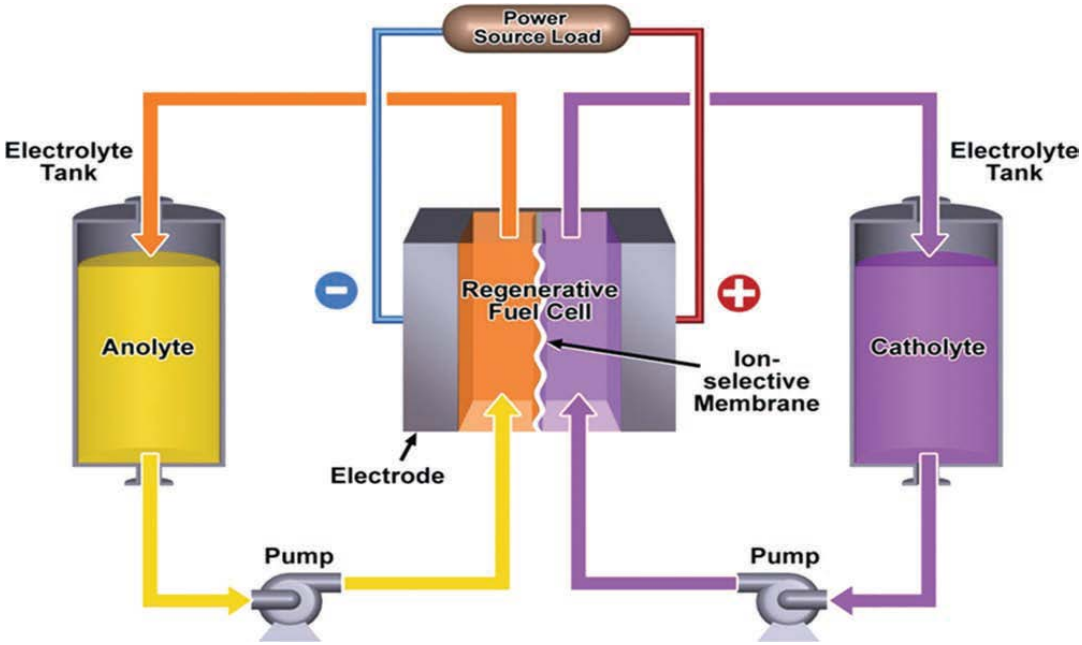

Fig. 4 - Flow battery working principle [15]

4.3.1 Zinc-bromine battery

Zinc-bromine battery is a type of hybrid flow battery. It uses two tanks full of zinc bromide($ZnBr_2$) water solution. Both tanks are filled with the same solution, one acts as a cathode and the other as anode. A section containing a polyolefin membrane connects the two tanks. The system requires pumps to circulate the solution past both electrode surfaces.

Electrical energy is stored in the form of electroplating zinc from the solution onto anode surface of the cell. At the same time, a reaction in which bromide changes into

bromine occurs at the cathode. During discharge, zinc and bromide ions are formed at the electrodes and the zinc plating on the anode dissolves and finishes the cycle.

Zinc-bromine batteries are easy to manufacture, offer high energy density and higher voltage of 1.8V because during the redox reaction, each atom of zinc releases two electrons. Their biggest limitation is low energy efficiency and short life-cycle. [16]

Anode reaction	$\mathbf{Zn^{2+} + 2e \rightarrow Zn_0}$	$E^0 = 0.763V$
Cathode reaction	$\mathbf{2Br^- \rightarrow Br_2(aq) + 2e}$	$E^0 = 1.087V$
Overall reaction	$\mathbf{ZnBr_2(aq) \rightarrow Zn^0 + Br(aq)}$	$E^0_{cell} = 1.85$

4.3.2 Vanadium redox

Vanadium redox battery uses two tanks filled with a vanadium-based electrolyte. The tanks are connected through a cell that is separated by a membrane. Pumps circulate the electrolyte through this cell to allow the exchange of ions.

A great deal of research and development was put into the all-vanadium redox flow battery, making it one of the most promising battery systems to date. Instead of employing two electroactive elements, VRB takes advantage of vanadium's ability to exist in four different oxidation states to create a redox pair. [15]

Anode reaction	$\mathbf{V^{2+} - e \rightarrow V^{3+}}$
Cathode reaction	$\mathbf{VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O}$
Overall reaction	$\mathbf{VO_2^+ + V^{2+} + 2H^+ \rightarrow VO^{2+} + V^{3+} + H_2O}$

VRB offers a cell voltage of 1.26V and an optimal temperature range between 10 to 40 °C. Although VRBs energy density is not as high as that of zinc-bromine, its

undisputable advantage is the extremely long life cycle, which is in the range of tens of thousands of cycles.

Wei Wang describes a major problem with present VRB applications as such:

"Traditional sulfuric-acid-based VRB technology is significantly hindered by the vanadium ion solubility and stability in electrolyte solutions over a certain temperature window" [15]

4.3.3 Polysulfide bromide battery (regenesys)

Polysulfide bromide battery is another well researched type of redox flow battery that is now somewhat obsolete, due to the large amount of research that is focused onto VRB. The working principle is identical to that of VRB, but it uses a solition of sodium bromide(NaBr) as the positive electrolyte and sodium polysulfide(Na_2S_x) as negative. [15]

Anode reaction $\mathbf{NaBr_3 + 2Na^+ + 2e \rightarrow 3NaBr}$

Cathode reaction $\mathbf{2Na_2S_2 \rightarrow Na_2S_4 + 2Na^+ + 2e}$

The principle of operation is taken from the 3rd edition of Handbook of Batteries:

"Sodium ions pass through the cation exchange membranes in the cells to provide electrolytic current flow and to maintain electroneutrality. The sulfur that would otherwise be produced in discharge dissolves in excess sodium sulfide that is present to form sodium polysulfide. The bromine produced at the positives on charge dissolves in excess sodium bromide to form sodium tribromide." [1]

A big advantage of all modern flow batteries and the reason why so much research has been done on them lately is that they are the optimal technology to use with electrical grids. Their ability to remain in a ready state for significant amount of time, thus offer a very *low self-discharge rate* makes them highly desirable for storing large amounts of el. energy for long time.

The downside is their *large volume* and fairly *low energy density* when compared with other battery systems. Flow batteries suffer from poor energy efficiency, averaging at around 77%. Although flow batteries are considered as stationary systems, some solutions were proposed to use them in electric vehicles, but their need for electrolyte circulation is a major obstacle.

Battery type	**Theoretical energy density**	**Achieved energy density**	**Potential**	**Efficiency**	**Self discharge rate**	**Temperature range**	**Cyles**
	Wh/Kg	Wh/Kg	V at 25 °C	charge/discharge	%/month	° C	80% capacity
Polysulfide bromide	41	15	1.36V	75%	5 - 10	10 - 50	1000 - 1500
Zinc-bromine	429	65 - 75	1.85V	68 - 73%	12 - 15 MAX	20 - 50	~2000
All-vanadium redox	372	10 - 20	1.26V	80 - 85%	5 - 10	10 - 40	50 000 - 80 000

Tab. 4.3.1 - Flow battery parameters [1] [15] [16]

5. Conclusion

In my bachelor's thesis, I have researched the current technologies of electrical energy storage, described their history, future and possibilities for each major type of battery listed. The introductory part deals with the fundamentals of electrical energy storage as well as the reasons why better batteries are crucially needed for future development. This includes the following: electric cars, fossil fuel reserves, renewable energy. The chapter also shows the possibilities of each currently used technology as well as their achieved limits, using the most recent data I was able to find.

In the first chapter, I have explained the theoretical principle of electrical energy storage in an electrochemical cell. Reduction-oxidation reaction is explained from both chemical and electrical perspective. The example given was lithium-Ion battery. Basic terms have been defined and explained in this chapter as well. The following chapters show each technology in more detail, starting with lithium batteries and proceed to other type of accumulators as well as some special cases such as fuel cells, supercapacitors and flow batteries each receiving their own separate chapter.

Even though the lithium-Ion battery was a major breakthrough in the field of energy storage, it was first commercially introduced more than 20 years ago and it is starting to show its technical limitations. The main part of my thesis described different energy storage methods that are split into three main sections that focus on most modern battery technologies. Each category included past, now deprecated type of battery, a currently used one and one or more technologies that are currently in a development stage.

Each of these new upcoming innovations in the field of energy storage is a pursuit of a better performing battery, one that is necessary if humanity wants to advance into the age of clean and renewable technology. An age without an internal combustion engine in every car. An age without the ever-present thermal power stations burning fossil fuels, slowly poisoning the whole planet. And an age we can all be proud of.

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